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EVALUATION OF THE RESIDUAL STABILITY OF POLYURETHANE AUTOMOTIVE COATINGS BY DSC

Equivalence of Xenotest and desert weathering tests and the synergism of stabilizers[*]

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Degradation of poly(ester-urethanes), poly(ether-urethanes) and poly(acrylic-urethanes), as a base for automotive paintings in interior applications, has been studied by DSC. The samples were clearcoat and black-pigmented paints, unstabilized and stabilized with HALS Tinuvin 292, UV absorber Tinuvin 1130 and antioxidant Hostanox O3, exposed to weathering in Xenotest and in Arizona desert. From the dependences of oxidation onset temperature on the heating rate, the kinetic parameters enabling to calculate the oxidation induction time for a chosen temperature have been obtained. From the values of oxidation induction time, the protection factors of the additives and the residual stability of the polymer after an ageing stress has been evaluated. It has been shown that the equivalence between the two methods of weathering depends on the polymer composition. A new criterion for the evaluation of synergism/antagonism of additives in the stabilizing mixture has been proposed.

Keywords: *accelerated ageing, automotive coating, DSC, polyurethane, residual stability, synergism, thermooxidation*

Introduction

The combination of oxygen as the reactant and heat as the energy source is a major factor in material degradation. Considering polyurethane (PUR), the effect of light on the rate of degradation should also be taken into account, since they are susceptible to photodegradation due to a high content of carbonyl groups [1]. The degradation leads to changes in the molecular structure and, consequently, to changes in the chemical and physical properties of materials. In most cases, the oxidation processes occurring in the condensed phase exhibit an induction period which is the stage preceding the main process, where apparently no chemical reaction takes place. The induction period of oxidation is determined as the time of a sudden increase in the oxidation rate. At the end of the induction period, often a sudden change of material characteristics occurs so that the length of induction period is frequently considered to be a measure of material stability. The induction periods, which are often used to compare polymer stabilities under given experimental conditions, play an important role in the prediction of long-term durability and service life. Two types of oxidative induction tests are introduced, the oxidative induction time (OIT) and the oxidative onset temperature (OOT) [2]. In the case of OIT, the sample is kept at a preset constant temperature and the time of sudden change of measured signal is detected. The OOT is determined as the onset temperature of oxidation reaction while the temperature is raised at a preset heating rate.

Automotive interior coatings are mostly two-component polyurethanes, the polyol component being commonly based on polyester or polyacrylic resins. Particularly softcoatings usually have a soft, leather-like feel and provide surfaces with improved haptic, acoustical and optical properties. The degradation of polyurethanes has been studied by many authors. Objects of the study were thermoplastics, foams, elastomers, aquatic dispersions and coatings. Crucial factors for the degradation of coatings for interior application are temperature and UV radiation. The influence of humidity is not so important as it is for exterior coatings. Kinetics of photo-oxidation of PUR coatings was studied by Mielewski *et al.* [3, 4]. Wilhelm *et al.* [5] suggested the mechanism of photodegradation for poly(ester-urethanes). It was shown

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[*] It is dedicated to Prof. Jona on the occasion of his 70th birthday

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that, upon irradiation at 320 nm, the degradation is brought about only by an induced oxidation of the urethane group where the polyester segments are relatively photostable. The primarily low photo-initiation rate for polyester coatings was found to increase with exposure time, suggesting that they undergo autocatalytic photooxidation. There are two different opinions about the degradation of poly(acrylic-urethanes). According to Mielewski *et al.* [3], the degradation of various acrylic polyurethanes is autocatalytic, i.e., the initial photoinitiation rate is low and the concentration of chromophores increases during exposure. Dudler *et al.* [6] could not observe a strictly defined induction period, which led them to the conclusion that the degradation does not occur through an autocatalytic mechanism. The photooxidation of poly(ether-urethanes) provides evidence for a dual mechanism. The polyether component is very sensitive to the induced photochemical oxidation, which leads to the formation of formates as the main photoproducts. The formates can be further oxidized and decompose to form low molecular weight products including ethylene and methyl formate [7].

In paper [8], a method of converting OOTs into OITs has been suggested and applied in follow-up studies to thermooxidation of edible oils, polyolefines, polyisoprene rubber and other materials as reviewed in [9]. The method has recently been applied to chemiluminescence study of thermooxidative degradation of polyurethane automotive coatings. Measurement of the residual stabilities of the coatings enabled to determine the equivalence of Xenotest and Solisi ageing tests [10]. In this paper, the degradation of poly(ester-urethane) (EST), poly(acrylic-urethane) (ACR) and poly(ether-urethane) (ETH) is studied by DSC. As mentioned above, automotive interior coatings are commonly based on polyester or polyacrylic resins. Polyether-polyol is also used as a resin for polyurethane, but for other applications; we included it to the study for completeness. The samples concerned are clearcoat and black-pigmented paints, unstabilized and stabilized with the eight possible combinations of radical scavenger (HALS), UV absorber (UVA) and antioxidant (AOX), exposed to various doses of accelerated ageing, i.e., Xenotest and desert weathering. The main aim of this paper is an evaluation of the residual stability of polyurethane automotive coatings by DSC, the equivalence of Xenotest and desert weathering tests and evaluation of the synergism between various stabilizers.

Kinetic analysis of reactions with induction period and evaluation of residual stability

In many cases, the determination of induction periods from isothermal measurements is quite difficult since the main oxidation stage of the process starts slowly so that its onset is not clearly recognisable and is hard to be determined unambiguously. This problem was also encountered during our chemiluminescence study of polyurethane thermooxidation [10]. Contrary to the isothermal measurements, in the nonisothermal measurements the start of the oxidation stage is clearer, the onset temperature can be read accurately and unambiguously. Hence, for the evaluation of polyurethane oxidation stabilities the nonisothermal DSC measurements were used. For the treatment of experimental data, the method for obtaining kinetic parameters of induction periods from the onset temperatures of nonisothermal DSC runs with linear temperature increase [8] was employed.

Within the single-step kinetics approximation [11], the rate of solid state processes can be described as a product of temperature and conversion functions:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{1}$$

where α is the conversion, $f(\alpha)$ is the conversion function and k stands for the temperature function. The temperature function is usually expressed by the Arrhenius equation. Equation (1) is assumed to hold for any solid-state process; hence, it should hold also for the processes occurring during the induction period. However, these processes are not detected by the technique used. The end of the induction period is determined indirectly as the oxidation onset temperature. It has been shown [8] that, for a series of measurements with linear heating rates, the dependence of OOT on the heating rate follows the relationship

$$\beta = \int_0^{T_i} \frac{\mathrm{d}T}{A\exp[B/T]} \tag{2}$$

where T_i is the oxidation onset temperature, β stands for the heating rate, A and B are constants and T is the absolute temperature. In the treatment of experimental results, A and B are adjustable parameters.

For isothermal degradation, the length of the induction period, t_i, is equal to OIT. It is expressed as the denominator of Eq. (2) [8]:

$$t_i = A\exp[B/T] \tag{3}$$

Equation (3) enables the calculation of OIT for a given temperature knowing the parameters A and B obtained from a dependence of the OOT on the heating rate.

In order to evaluate the protective effect of stabilizers added, it was suggested to use the protection factor (*PF*) [9, 12]:

$$PF = \frac{t_{\mathrm{i}}\,(\mathrm{stab})}{t_{\mathrm{i}}\,(\mathrm{unstab})} \tag{4}$$

where t_{i}(stab) and t_{i}(unstab) are the induction periods of stabilized and unstabilized polymer, respectively. If $PF>1$, the additive has a stabilizing effect on the polymer; otherwise, the additive has a destabilizing effect. The greater the *PF* value, the higher the stabilizing effect of the additive.

The OIT is understood a measure of oxidation stability. In [8], the concept of depleted and residual stabilities has been introduced. The sum of both stabilities is equal to one. For an isothermal process, the residual stability, *R*, can be evaluated as

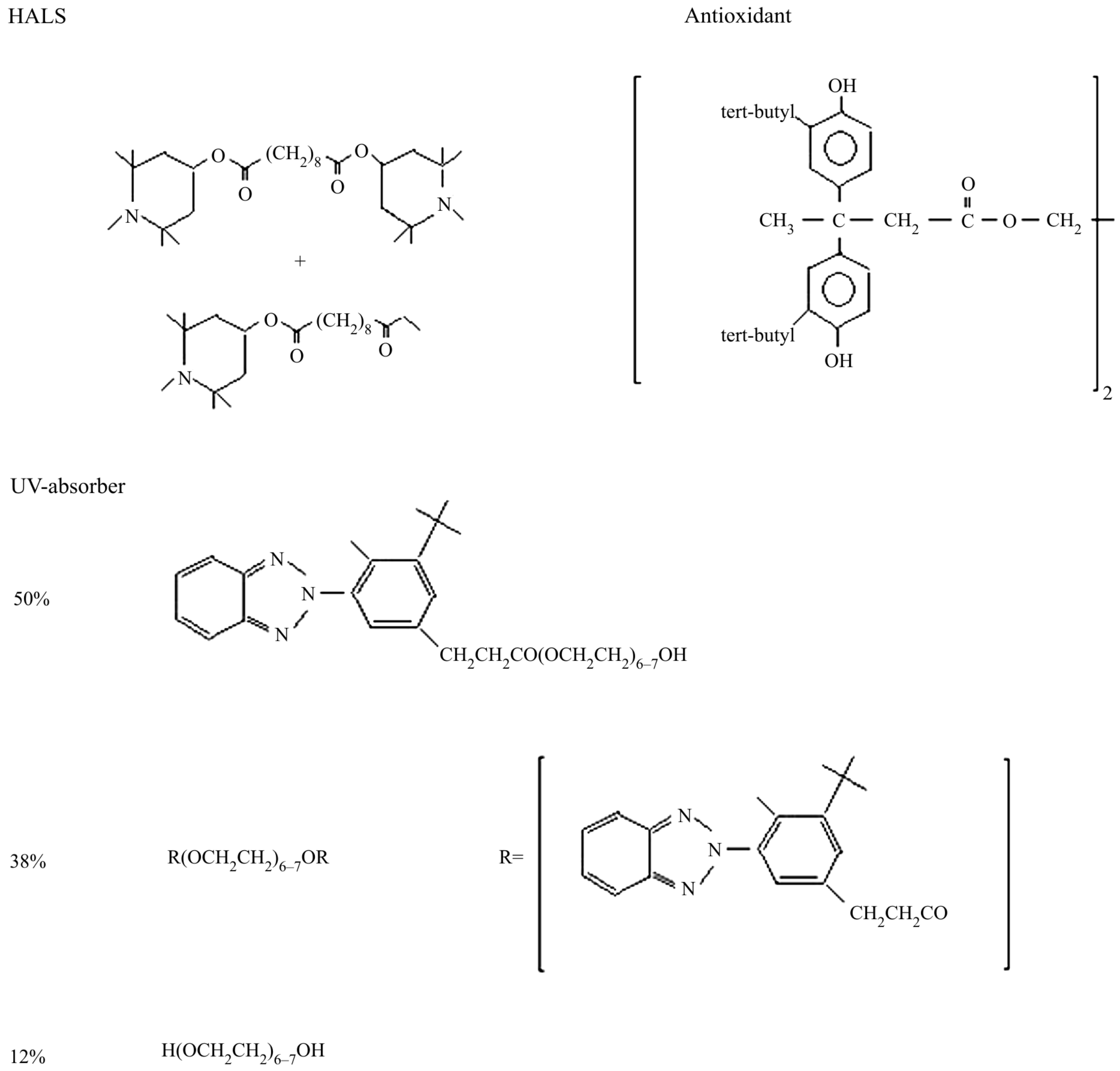
$$R = \frac{t_{\mathrm{i}}}{t_{\mathrm{io}}} \tag{5}$$

where t_{i} is the OIT of the sample after the ageing stress and t_{io} is the OIT of the unstressed sample. It has been shown [10], that the decrease in residual stability with the ageing dose can be approximated by a first-order relationship

$$R = \exp[-a_{\mathrm{k}}d_{\mathrm{k}}] \tag{6}$$

where a_{k} is the extinction constant of residual stability and d_{k} is the ageing dose, the index *k* is related to the method of ageing. For a zero ageing dose (non-weathered samples), the residual stability calculated by Eq. (6) is equal to 1.

Provided that the values of a_{k1} and a_{k2} are known, one can make a guess on the equivalence of two weathering methods considering the ageing se-



Scheme 1 Structures of HALS, UV absorber and antioxidant

verity. If the sample is exposed to an equivalent ageing dose in both methods, its residual stability should have the same value. This consideration can be mathematically written as

$$\exp[-a_{k1}d_{k1}] = \exp[-a_{k2}d_{k2}] \tag{7}$$

The equivalence of both methods can be expressed as [10]

$$e = \frac{d_{k2}}{d_{k1}} = \frac{a_{k1}}{a_{k2}} \tag{8}$$

Experimental

Materials

The samples are two-component, solvent-based polyurethane films prepared from polyester (content of OH groups 4.3%), polyacrylic (2.8%) and polyether (26.8%) resin and one type of hardener (aliphatic polyisocyanate based on HDI, content of NCO groups 16.5%) in the ratio NCO:OH=1:1. The catalyst, containing the active component di-*n*-butyltinmercaptid, was used in the concentration 0.5 mass% to the amount of resin. Black pigment paste consists of 50 mass% of carbon black and 50 mass% of solvent. The amount of added paste was 10 mass% to the amount of resin. Three types of stabilizers were added, i.e. HALS Tinuvin 292 (Ciba, Switzerland), UV absorber Tinuvin 1130 (Ciba, Switzerland) and antioxidant Hostanox O3 (Clariant, France) (Scheme 1). The amounts of stabilizers added are given in Table 1. A film thickness of 60 μm was applied onto glass plates and cured at 80°C for 2 h, then followed for 24 h at room temperature.

DSC instrumentation

A Mettler Toledo 821 DSC calorimeter was employed for the study of thermooxidation stability of the samples. The temperature scale was calibrated using In and Sn. The film samples (1–1.3 mg) were placed in standard aluminium pans, where the lid of each pan was perforated by 7 pinholes. The samples were examined under oxygen atmosphere within the temperature range 50–250°C at heating rates of 1, 3, 5, 7, 10 and 15 K min^{-1}.

Weathering conditions

The samples were exposed to an artificial weathering using Xenotest Beta LM (Atlas, Germany) for various numbers of periods. The period is a specified dose of irradiance defined by DIN 75202. According to [13], five periods simulate one year of weathering under hot-dry desert conditions. The device was equipped with xenon lamps and operated at following conditions: cut-off of the simulated solar radiation at 320 nm, 60 W m^{-2} irradiance in spectral range 280–400 nm, 65°C sample-space temperature and 100°C black standard temperature.

Natural weathering in extreme conditions is another type of accelerated material tests. We exposed the samples in Arizona desert for one year in a glass box, situated 5° to the northwest. One year in such conditions (hot-dry) should simulate 4–5 years in the Middle-European climate.

Results and discussion

Kinetic parameters and lengths of induction periods

The OOT was determined from a DSC record as the onset of the oxidation peak. An example of a DSC re-

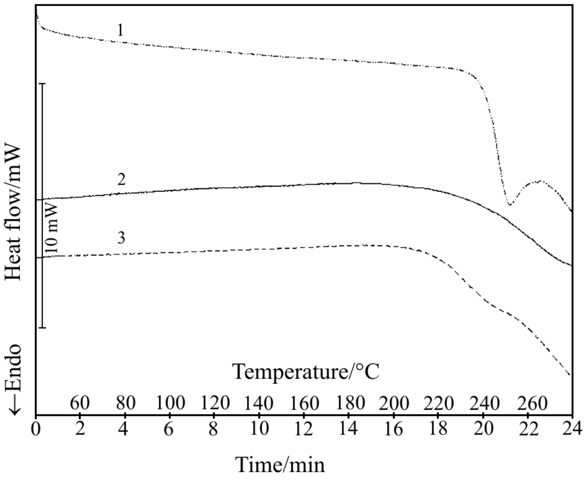


Fig. 1 DSC runs for oxidation of poly(ester-urethane), stabilized with HALS+AOX, black-pigmented, oxygen, heating rate 10 K min^{-1}: 1 – unexposed; 2 – after exposure 5 periods in Xenotest; 3 – after exposure 1 year in desert

Table 1 Amounts of additives in PUR coatings expressed as the number of parts added per hundred parts of resin

Stabilizer	Label							
	none	HALS	UVA	AOX	HALS+UVA	HALS+AOX	UVA+AOX	All
HALS	–	1	–	–	0.7	1	–	0.7
UVA	–	–	1	–	0.3	–	1	0.3
AOX	–	–	–	1	–	1	1	1

Table 2 Oxidation onset temperatures (in °C) for poly(ester-urethane) as a function of the heating rate. 0 – sample without aging stress; X2.5 and X5 – weathering 2.5 and 5 periods in Xenotest, respectively; D0.5 and D1 – weathering 0.5 and 1 year in desert, respectively

Stabilizer/aging	Heating rate/K min^{-1}											
	poly(ester-urethane) clear						poly(ester-urethane) black					
	1	3	5	7	10	15	1	3	5	7	10	15
none/0	180.5	188.5	197.2	203.7	209.6	214.5	179.0	195.3	203.6	205.2	211.4	217.5
none/X2.5	163.7	175.1	180.2	186.3	187.7	194.8	171.3	178.7	185.0	190.0	194.7	199.3
none/X5	161.3	172.0	175.6	178.8	184.1	186.4	165.7	173.3	178.0	186.7	191.9	199.9
none/D0.5	173.7	175.1	176.9	179.6	192.9	196.6	177.6	178.2	185.2	190.5	195.7	200.1
noe/D1	171.1	172.5	178.9	187.9	190.5	192.3	173.6	176.2	181.8	184.4	186.2	192.0
HALS/0	202.2	212.7	224.6	230.6	236.2	240.5	210.2	221.5	228.2	235.9	238.7	248.5
HALS/X2.5	188.8	201.0	207.8	212.0	220.3	224.1	195.9	203.5	210.5	218.6	224.7	233.1
HALS/X5	183.2	198.7	205.9	209.4	213.5	220.5	191.1	199.3	206.2	209.6	215.8	220.3
HALS/D0.5	205.4	214.8	225.7	227.4	238.2	238.6	–	–	–	–	–	–
HALS/D1	202.4	211.5	223.5	224.8	232.8	238.0	–	–	–	–	–	–
UVA/0	176.5	188.8	194.7	200.2	204.2	211.0	181.9	189.3	198.2	208.9	210.3	223.6
UVA/X2.5	164.1	173.0	176.6	182.1	187.7	193.0	170.2	180.1	185.6	200.7	205.0	214.6
UVA/X5	161.8	172.8	174.5	181.7	186.7	192.5	165.7	177.1	183.1	188.0	193.2	200.0
UVA/D0.5	171.2	180.4	182.7	182.8	190.3	196.5	178.3	184.9	187.4	194.8	197.3	201.5
UVA/D1	171.9	178.8	180.9	181.4	190.2	195.1	176.1	177.3	181.5	184.5	187.5	190.1
AOX/0	206.8	220.9	231.5	234.5	242.3	246.8	206.6	224.2	231.4	234.8	243.7	250.1
AOX/X2.5	192.7	206.0	215.1	217.0	221.6	227.9	202.5	214.8	221.0	226.7	231.2	236.6
AOX/X5	192.0	202.4	207.9	210.1	212.7	218.7	193.5	206.5	214.3	218.6	220.4	226.1
AOX/D0.5	194.3	202.2	207.9	221.0	225.1	231.3	194.7	199.1	207.1	211.5	215.9	220.6
AOX/D1	179.9	197.0	206.5	217.2	221.8	228.6	188.6	195.1	200.0	207.4	211.2	219.4
HALS+UVA/0	208.1	217.6	226.9	237.0	237.3	243.5	214.0	224.1	231.3	239.2	242.1	247.3
HALS+UVA/X2.5	205.3	215.0	217.3	225.6	229.5	232.6	209.2	219.6	221.5	228.6	234.4	238.1
HALS+UVA/X5	202.3	214.6	215.3	219.8	227.6	230.0	201.7	212.4	214.6	217.6	224.1	228.9
HALS+UVA/D0.5	207.2	211.5	223.5	230.6	232.1	237.0	212.1	222.0	227.6	235.8	239.2	243.7
HALS+UVA/D1	205.3	208.1	221.3	227.9	230.9	232.4	206.1	216.4	220.6	225.3	228.1	231.9
HALS+AOX/0	213.7	223.2	237.6	241.9	249.7	255.5	224.0	231.3	242.5	247.1	251.6	258.4
HALS+AOX/X2.5	202.3	227.6	227.8	231.8	237.2	243.4	209.5	218.3	225.8	227.9	233.4	240.5
HALS+AOX/X5	199.0	213.1	221.3	227.2	229.5	237.0	207.1	216.5	222.5	226.6	231.7	236.9
HALS+AOX/D0.5	206.5	219.8	235.0	236.5	239.9	244.8	220.5	228.2	236.1	238.1	243.3	245.7
HALS+AOX/D1	200.9	222.2	225.2	228.2	236.4	239.1	202.8	223.4	226.9	230.2	237.9	241.0
UVA+AOX/0	213.7	228.7	239.4	246.2	251.2	257.8	210.4	224.8	230.0	237.7	239.9	245.4
UVA+AOX/X2.5	195.2	209.3	215.7	220.4	223.4	231.5	204.9	214.6	220.3	224.7	230.9	234.9
UVA+AOX/X5	185.2	200.0	203.7	211.3	214.4	220.7	195.5	206.6	213.2	215.3	218.7	227.0
UVA+AOX/D0.5	182.8	205.7	209.7	216.4	222.7	227.1	193.5	202.5	210.8	217.9	220.9	225.6
UVA+AOX/D1	178.7	192.1	200.4	211.7	218.0	226.6	181.8	199.8	208.1	212.7	217.7	219.4
AII/0	216.8	230.7	238.9	244.8	248.7	257.8	220.1	227.9	230.4	237.2	239.2	241.7
AII/X2.5	203.7	219.6	226.6	232.2	237.1	243.1	207.6	215.3	221.9	226.5	229.6	232.4
AII/X5	198.7	214.0	222.0	226.8	233.0	240.6	204.5	214.3	221.6	224.8	228.6	230.7
AII/D0.5	215.6	224.6	233.0	236.9	238.9	244.9	216.9	224.9	227.8	235.2	237.6	239.4
AII/D1	210.2	222.1	232.9	235.5	238.0	241.8	211.3	223.4	224.6	232.5	236.4	238.0

Table 3 Oxidation onset temperatures (in °C) for poly(ether-urethane) as a function of the heating rate. 0 – sample without aging stress; X5 – weathering 5 periods in Xenotest, D1 – weathering 1 year in desert

Stabilizer/aging	Heating rate/K min^{-1}											
	poly(ether-urethane) clear						poly(ether-urethane) black					
	1	3	5	7	10	15	1	3	5	7	10	15
none/0	175.1	189.8	189.7	193.9	196.3	199.6	179.2	186.7	195.3	187.0	189.7	203.7
none/X5	170.5	181.8	182.6	185.0	188.4	195.1	174.0	185.7	185.9	181.8	184.4	195.5
none/D1	176.7	180.6	182.7	184.2	191.3	198.2	170.5	176.4	179.8	173.4	178.1	193.0
HALS/0	205.3	219.3	226.1	233.2	236.1	239.7	205.7	221.6	227.2	218.2	222.3	239.8
HALS/X5	201.9	215.0	220.5	224.7	227.0	229.9	198.8	215.7	220.6	211.7	216.0	228.9
HALS/D1	205.5	215.2	221.0	223.4	228.5	232.4	194.1	204.2	208.4	199.1	206.3	226.8
UVA/0	186.0	200.8	207.6	212.0	216.7	222.2	185.4	200.1	209.9	198.5	202.8	223.2
UVA/X5	174.5	180.2	186.1	190.1	194.4	197.9	170.4	177.5	181.1	176.3	178.3	193.0
UVA/D1	172.8	180.7	187.8	189.8	193.8	196.4	173.2	182.5	184.4	177.8	183.4	198.0
AOX/0	191.5	205.5	209.4	218.2	220.9	226.5	191.8	207.2	214.9	204.6	208.9	229.8
AOX/X5	181.8	183.1	185.5	189.7	192.7	203.7	181.0	187.5	190.3	186.3	188.0	202.9
AOX/D1	180.8	188.5	197.2	202.3	205.7	208.8	181.3	185.0	192.8	183.1	188.9	200.0
HALS+UVA/0	204.2	218.3	224.6	229.8	233.8	238.6	201.7	214.6	223.7	213.3	217.2	235.9
HALS+UVA/X5	199.3	211.4	218.9	221.2	225.3	228.4	199.8	212.0	217.0	209.6	212.9	230.7
HALS+UVA/D1	200.1	211.7	219.6	221.4	225.9	233.0	196.1	201.2	214.2	198.6	207.7	219.4
HALS+AOX/0	206.6	223.3	228.7	235.5	238.8	240.8	205.9	221.7	228.1	218.6	222.8	240.7
HALS+AOX/X5	205.4	220.1	226.9	230.7	234.5	238.3	202.2	214.7	219.3	212.0	215.3	230.3
HALS+AOX/D1	204.7	218.6	225.1	228.0	233.3	235.2	202.4	215.9	218.2	209.2	217.1	227.1
UVA+AOX/0	194.0	207.6	210.6	218.5	223.5	231.4	194.1	206.0	213.6	204.5	208.0	232.1
UVA+AOX/X5	183.2	191.6	195.9	197.3	200.4	211.6	182.3	186.6	194.4	187.6	189.6	211.0
UVA+AOX/D1	182.1	195.0	197.6	202.1	205.4	212.2	182.5	188.8	195.5	185.6	192.1	206.8
AII/0	206.6	220.6	226.5	232.5	235.7	241.2	208.6	221.6	225.8	218.6	222.0	242.2
AII/X5	202.8	215.4	222.5	226.2	231.5	236.0	204.6	212.5	221.0	212.7	215.4	235.5
AII/D1	204.6	210.0	218.3	219.9	227.2	230.4	203.1	209.2	218.5	206.1	213.8	225.1

cord is shown in Fig. 1. The OOTs for all measured systems are given in Tables 2–4. Considering the dependence of OOT on the heating rate, the kinetic parameters A and B were obtained using Eq. (2) by minimising the sum of squares between experimental and calculated values of oxidation onset temperatures by the simplex method. The values of A and B are listed in Tables 5–7.

Equation (3) indicates that the lengths of induction periods depend on temperature. In thermooxidation tests of polymers, the temperature of 180°C is very often used. Consequently, OITs for this temperature were calculated from the parameters A and B using Eq. (3); their values are listed in Tables 5–7. The value of OIT represents a relative measure of the thermooxidative stability [9]. As can be seen from Tables 5–7, the most stable unstabilized system before weathering is EST whereas ACR is the most stable system after weathering either in Xenotest or in desert. This indicates that acrylic segments are more resistant towards degradation than polyether or ester segments. The most stable system after stabilization with all three stabilizers is EST system (the only exception is black-pigmented ACR before weathering). This is an indication that the mixture of all three stabilizers is suitable mainly for EST.

Protection factors

The protection factor is a ratio of OITs of stabilized and unstabilized polymer. It is an evaluation of the protective effect of stabilizers added. The protection factors, calculated for 180°C using Eq. (4), are shown in Table 8. The OIT of unstabilized sample after weathering was used as the value of t_i(unstab) for each weathering dose.

The data in Table 8 reveal that the protection factors depend much on the weathering dose. It increases or remains unchanged with the ageing dose for all systems when stabilized with HALS. When stabilized

Table 4 Oxidation onset temperatures (in °C) for poly(acrylic-urethane) as a function of the heating rate. 0 – sample without aging stress; X5 – weathering 5 periods in Xenotest, D1 – weathering 1 year in desert

Stabilizer/aging	Heating rate/K min^{-1}											
	poly(acrylic-urethane) clear						poly(acrylic-urethane) black					
	1	3	5	7	10	15	1	3	5	7	10	15
none/0	177.0	182.9	188.3	196.0	199.7	205.3	175.2	182.1	192.6	194.6	203.4	208.6
none/X5	166.0	172.3	182.1	186.4	190.5	200.7	173.2	182.9	186.0	188.7	193.6	200.6
none/D1	167.0	178.4	185.6	187.4	194.0	199.1	172.7	181.9	186.3	187.6	192.3	199.5
HALS/0	183.9	189.3	196.3	207.8	208.8	216.9	183.9	197.0	203.8	211.0	213.7	218.9
HALS/X5	178.5	185.8	193.9	204.4	208.9	213.9	187.3	197.4	204.2	211.7	218.0	220.3
HALS/D1	183.8	188.2	192.7	197.0	204.4	212.3	179.4	185.9	190.8	192.7	201.4	202.7
UVA/0	186.7	194.7	201.8	208.2	214.3	220.1	184.8	192.4	204.6	204.9	206.0	213.0
UVA/X5	172.2	174.8	182.7	192.1	194.5	201.3	172.3	186.0	188.4	193.4	199.6	205.2
UVA/D1	169.3	181.1	189.4	190.2	192.8	196.5	174.5	185.5	188.9	190.7	193.2	197.6
AOX/0	203.4	213.8	223.9	225.6	230.0	236.4	205.1	215.2	222.8	231.6	234.7	239.1
AOX/X5	190.0	205.7	212.6	213.8	214.8	222.1	193.5	203.9	207.7	215.0	218.1	220.2
AOX/D1	178.5	190.0	192.0	193.0	197.8	212.9	184.6	192.3	194.3	199.9	207.0	218.7
HALS+UVA/0	186.3	201.6	208.8	210.2	217.1	223.0	193.5	197.9	204.6	207.0	215.1	217.3
HALS+UVA/X5	185.7	193.2	198.2	202.9	207.2	213.0	185.3	195.4	203.2	205.7	210.4	214.6
HALS+UVA/D1	180.3	189.6	195.4	200.9	203.7	212.6	181.2	196.2	197.7	200.0	203.6	213.3
HALS+AOX/0	208.9	219.3	227.4	228.5	235.3	239.7	218.4	223.5	230.5	236.8	240.2	243.7
HALS+AOX/X5	204.5	209.4	220.4	220.6	223.9	224.8	205.8	212.2	221.9	223.4	228.7	235.2
HALS+AOX/D1	206.1	212.9	220.2	221.9	226.3	232.4	206.5	214.5	223.9	226.4	230.9	236.1
UVA+AOX/0	206.6	218.9	225.9	230.7	233.1	239.6	210.2	225.4	231.7	235.5	238.4	243.2
UVA+AOX/X5	203.3	208.8	216.1	219.7	222.9	229.0	200.3	211.8	218.0	219.4	221.3	230.5
UVA+AOX/D1	201.5	198.6	212.2	214.8	221.3	223.3	191.3	202.8	208.4	216.9	223.7	230.2
All/0	212.4	220.2	224.9	228.9	234.6	238.9	213.7	219.5	226.9	233.5	235.5	240.7
All/X5	204.7	208.3	214.0	217.9	227.4	230.8	200.2	204.7	212.9	218.4	224.7	229.1
All/D1	205.8	210.4	213.5	214.7	219.0	222.9	198.4	201.5	210.7	219.3	225.8	230.4

with all three stabilizers, *PF* increases with the ageing dose for EST and ETH and decreases for ACR, both for clearcoat and black-pigmented systems and both for Xenotest and desert weathering. This indicates the unsuitability of the used mixture of all three stabilizers for ACR stabilization.

Residual stability, extinction constants and equivalence of both methods of accelerated ageing

For a given sample, the residual stability is a ratio of OITs after and before weathering. For an unaged sample, the residual stability is equal to one. The residual stability decreases with increasing the ageing dose; at the end of the lifetime after ageing, the residual stability is close to zero. The residual stabilities were obtained from the data of Tables 5–7 using Eq. (5); their values are not presented here. Subsequently, the extinction constants of residual stability for Xenotest and desert weathering, a_X and a_D, were calculated using Eq. (6); their values are also listed in Table 9.

The extinction constants express the susceptibility of a polymer to ageing. The higher the value of the constant, the greater the susceptibility is. As seen from Table 9, the extinction constants depend much on the composition of the polymer system. For the Xenotest ageing, EST polymers exhibit the highest values of extinction constants, both clearcoat and black-pigmented polymers. This fact points out that the conditions in Xenotest weathering are very severe for EST. The trend in ageing susceptibility for Xenotest weathering is EST>ETH>ACR. For the desert weathering, extremely high extinction constants (above 1 yr^{-1}) are seen for EST unstabilized and stabilized with AOX, UVA and AOX+UVA, both for clearcoat and black-pigmented systems. For the systems containing the mixture of all three stabilizers, the trend in ageing susceptibility is ACR>ETH>EST.

Table 5 Kinetic parameters of the induction periods for poly(ester-urethane) obtained from the treatment of data in Table 2 using Eq. (2) and the oxidation induction times at 180°C calculated by Eq. (3) [min]

Sample/aging	poly(ester-urethane) clear			poly(ester-urethane) black		
	A/min	$10^{-3}B$/K	t_i (180°C)/min	A/min	$10^{-3}B$/K	t_i (180°C)/min
none/0	1.74E-13	14.36	10.0	4.00E-14	15.14	12.9
none/X2.5	2.46E-15	15.67	2.6	4.60E-16	16.61	3.8
none/X5	3.47E-20	20.42	1.3	3.04E-11	11.53	3.5
none/D0.5	1.61E-12	12.81	3.0	2.53E-16	16.92	4.1
none/D1	3.67E-19	19.65	2.5	1.10E-20	21.17	2.1
HALS/0	4.99E-15	16.92	82.8	1.32E-14	16.60	107.1
HALS/X2.5	7.11E-14	15.09	20.5	3.95E-11	12.25	21.8
HALS/X5	1.28E-14	15.77	16.6	4.77E-16	17.35	20.4
HALS/D0.5	1.61E-15	17.45	85.3	–	–	–
HALS/D1	2.43E-15	17.15	66.3	–	–	–
UVA/0	4.81E-14	14.84	8.0	3.33E-09	9.89	10.1
UVA/X2.5	1.64E-14	14.76	2.3	1.58E-11	12.13	6.7
UVA/X5	5.92E-14	14.16	2.2	3.89E-13	13.53	3.6
UVA/D0.5	1.54E-15	15.94	2.9	9.47E-16	16.46	5.6
UVA/D1	8.58E-16	16.17	2.7	9.57E-16	16.13	2.8
AOX/0	7.59E-15	16.90	119.4	8.98E-15	16.85	126.5
AOX/X2.5	8.75E-16	17.32	35.0	9.25E-16	17.61	70.0
AOX/X5	2.22E-19	20.96	27.3	1.37E-18	20.41	49.6
AOX/D0.5	5.68E-12	13.17	23.8	1.30E-17	19.09	25.9
AOX/D1	4.79E-11	12.06	17.4	2.63E-18	19.67	18.7
HALS+UVA/0	8.9E-19	21.25	117.9	9.61E-16	18.00	171.3
HALS+UVA/X2.5	9.01E-16	17.58	63.6	6.92E-17	18.97	104.9
HALS+UVA/X5	9.18E-16	17.48	51.9	8.99E-19	20.92	100.8
HALS+UVA/D0.5	9.12E-16	17.68	80.2	6.81E-17	19.19	167.6
HALS+UVA/D1	9.10E-16	17.58	64.2	4.51E-21	23.50	150.0
HALS+AOX/0	1.14E-12	14.60	112.0	9.14E-15	17.21	284.9
HALS+AOX/X2.5	3.32E-14	16.10	89.4	1.89E-19	21.87	172.5
HALS+AOX/X5	1.18E-14	16.36	56.2	1.06E-16	18.69	87.4
HALS+AOX/D0.5	1.61E-15	17.65	95.8	2.83E-17	19.83	285.7
HALS+AOX/D1	4.24E-15	17.00	83.2	6.78E-17	19.10	136.3
UVA+AOX/0	2.01E-12	14.40	127.1	3.55E-15	17.30	135.1
UVA+AOX/X2.5	2.27E-15	17.00	44.5	1.23E-16	18.56	75.3
UVA+AOX/X5	4.72E-15	16.26	18.1	2.44E-18	20.09	43.8
UVA+AOX/D0.5	3.08E-12	13.40	21.4	1.52E-16	18.11	34.4
UVA+AOX/D1	1.04E-10	11.60	13.6	5.24E-19	20.64	31.6
AII/0	2.63E-14	16.58	204.3	9.14E-15	17.21	284.9
AII/X2.5	3.47E-14	16.03	80.1	1.89E-19	21.87	172.5
AII/X5	2.56E-13	14.92	50.9	4.66E-19	21.35	135.0
AII/D0.5	1.38E-16	18.9	179.6	2.83E-17	19.83	235.7
AII/D1	5.54E-17	19.26	159.2	4.66E-19	21.50	187.8

The equivalence of ageing methods was first introduced in our previous paper [10]. For a given sample, the equivalence can be obtained as a ratio of the extinction coefficients for two ageing methods by using Eq. (8). The values of equivalence are listed in Table 9. The arithmetic mean of all the values in

Table 6 Kinetic parameters of the induction periods for poly(ether-urethane) obtained from the treatment of data in Table 3 using Eq. (2) and the oxidation induction times at 180°C calculated by Eq. (3) [min]

Sample/aging	poly(ether-urethane) clear			poly(ether-urethane) black		
	A/min	$10^{-3}B$/K	t_i (180°C)/min	A/min	$10^{-3}B$/K	t_i (180°C)/min
none/0	3.83E-21	2.21E+04	5.7	1.82E-19	20.47	7.6
none/X5	1.81E-21	2.21E+04	2.7	8.88E-24	24.65	3.7
none/D1	1.79E-21	2.22E+04	3.2	8.23E-21	21.3	2.1
HALS/0	3.69E-16	1.82E+04	109.2	1.24E-16	18.78	123.2
HALS/X5	3.78E-17	1.91E+04	74.7	9.97E-19	20.75	76.8
HALS/D1	4.05E-18	2.02E+04	92.6	9.96E-19	20.5	44.2
UVA/0	5.68E-15	1.62E+04	20.4	3.13E-14	15.46	20.5
UVA/X5	1.46E-20	2.13E+04	3.9	5.26E-21	21.57	2.5
UVA/D1	3.04E-21	2.20E+04	3.8	1.00E-21	22.43	3.1
AOX/0	6.78E-16	1.74E+04	31.4	5.41E-14	15.43	33.2
AOX/X5	9.57E-23	2.37E+04	5.1	1.78E-20	21.47	6.7
AOX/D1	9.42E-19	1.99E+04	10.4	4.93E-25	26.21	6.5
HALS+UVA/0	2.92E-16	1.83E+04	96.5	1.48E-15	17.4	70.2
HALS+UVA/X5	1.44E-19	2.16E+04	79.2	9.24E-18	19.68	67.1
HALS+UVA/D1	8.06E-18	1.98E+04	69.9	2.72E-23	25.3	48.1
HALS+AOX/0	2.92E-16	1.84E+04	134.6	1.93E-16	18.58	124.0
HALS+AOX/X5	2.82E-17	1.95E+04	123.1	9.98E-19	20.78	82.1
HALS+AOX/D1	3.47E-16	1.82E+04	94.2	9.96E-19	20.77	80.2
UVA+AOX/0	1.98E-15	1.70E+04	36.4	1.45E-14	16.04	34.1
UVA+AOX/X5	1.90E-19	2.06E+04	10.1	2.72E-19	20.28	7.4
UVA+AOX/D1	1.70E-18	1.97E+04	12.3	3.70E-21	22.31	8.9
AII/0	4.47E-16	1.82E+04	110.9	3.27E-16	18.3	112.9
AII/X5	9.58E-17	1.87E+04	83.6	1.37E-17	19.62	87.4
AII/D1	1.81E-18	2.05E+04	75.3	2.75E-20	22.4	80.9

Table 9 indicates that 5.4 Xenotest periods are equivalent to one year of desert ageing. This value is in a very good agreement with the value of 5 period/yr mentioned in [13]. However, the values of equivalence are very scattered as demonstrated by the value of standard deviation which is 2.1 period/yr. The equivalence obviously depends on the composition of the system. The lowest values below 2 period/yr are seen for EST coatings stabilized with the mixture of all three additives. The highest value, about 10 Xenotest periods per one year of desert ageing, exhibits the black-pigmented ETH coating stabilized with HALS. The data of Table 9 show that the dependence of equivalence on the composition is complicated. A similar fact was observed for the equivalence of Xenotest and Solisi weathering studied by chemiluminescence [10].

Stabilizer effectiveness and stabilizer synergism

In [9, 12] it has been suggested to evaluate the antioxidant effectiveness, *AEX*, by the relationship

$$AEX = \frac{PF - 1}{X} \tag{9}$$

where X is expressed as the number of parts added per hundred parts of resin (phr). It is a matter of course that the effectiveness of any stabilizer or additive can be evaluated by Eq. (9), not only the effectiveness of antioxidants. The stabilizer effectiveness means an increment of the protection factor brought about by the additives, related to 1 phr of the additives. If *AEX* is positive, the additive increases the polymer stability. A negative value of *AEX* indicates that the additive has a pro-degradation effect. The values of stabilizer effectiveness are summarized in Table 10. The highest values exhibit mostly the EST-based systems. The trend for EST and ETH systems is that the black pigment reduces the stabilizer effectiveness.

Polymers are generally stabilized by a mixture of stabilizers. Due to the interaction between stabilizers, the stabilizing effect of the mixture can be enhanced or reduced in comparison with the effect of individual stabilizers which is termed as the synergism or antag-

Table 7 Kinetic parameters of the induction periods for poly(acrylic-urethane) obtained from the treatment of data in Table 4 using Eq. (2) and the oxidation induction times at 180°C calculated by Eq. (3) [min]

Sample/aging	poly(acrylic-urethane) clear			poly(acrylic-urethane) black		
	A/min	$10^{-3}B$/K	t_i (180°C)/min	*A*/min	$10^{-3}B$/K	t_i (180°C)/min
none/0	7.49E-15	15.53	5.7	1.09E-12	13.32	6.3
none/X5	5.26E-11	11.30	3.5	3.05E-15	15.77	3.9
none/D1	6.13E-15	15.41	3.6	1.39E-15	16.09	3.7
HALS/0	1.57E-12	13.38	10.4	4.18E-16	17.37	18.5
HALS/X5	9.97E-13	13.52	9.1	7.93E-15	16.04	18.8
HALS/D1	2.51E-12	13.01	7.4	4.35E-17	17.87	5.8
UVA/0	3.28E-13	14.21	13.8	1.61E-18	19.78	14.7
UVA/X5	2.16E-13	13.85	4.0	2.50E-14	14.96	5.4
UVA/D1	8.94E-25	25.73	4.1	5.24E-24	24.96	4.4
AOX/0	3.58E-16	18.07	74.0	4.09E-16	18.13	96.4
AOX/X5	4.45E-19	20.78	36.3	3.19E-21	23.13	46.9
AOX/D1	6.32E-10	10.43	6.3	4.84E-10	10.69	8.5
HALS+UVA/0	1.38E-14	15.82	20.0	3.93E-19	20.65	24.3
HALS+UVA/X5	4.55E-16	17.10	11.1	5.58E-19	20.34	17.4
HALS+UVA/D1	6.72E-10	10.46	7.0	5.51E-19	20.18	12.1
HALS+AOX/0	3.55E-17	19.35	125.8	5.59E-20	22.78	379.9
HALS+AOX/X5	3.85E-21	23.39	100.4	5.32E-20	22.30	125.2
HALS+AOX/D1	3.99E-19	21.27	96.9	1.04E-20	23.18	170.8
UVA+AOX/0	5.76E-17	19.10	115.4	2.30E-20	23.19	384.1
UVA+AOX/X5	1.20E-17	19.46	53.2	1.66E-19	21.53	71.3
UVA+AOX/D1	1.75E-18	20.21	41.0	1.02E-11	12.84	20.8
All/0	6.58E-18	20.16	138.8	1.64E-18	20.94	189.6
All/X5	1.40E-14	16.09	37.2	4.06E-18	19.93	51.2
All/D1	4.02E-19	20.64	24.3	4.92E-13	14.34	27.2

Table 8 Protection factors at 180°C for various stabilizers and various aging stress

Stabilizer	poly(ester-urethane)					poly(ether-urethane)			poly(acrylic-urethane)		
clear	0	X2.5	X5	D0.5	D1	0	X5	D1	0	X5	D1
HALS	10.7	31.1	47.4	29.1	33.4	22.7	44.1	36.9	2.2	3.1	3.0
UVA	0.8	0.9	1.7	1.0	1.1	3.6	1.5	1.2	2.8	1.3	1.2
AOX	13.8	13.5	21.0	7.9	7.0	5.5	1.9	3.3	13.2	8.6	2.4
HALS+UVA	20.7	38.4	60.0	43.7	40.3	19.8	29.3	21.8	3.5	4.4	3.0
HALS+AOX	12.5	30.4	42.9	36.7	34.1	23.6	45.6	36.0	30.8	36.2	32.4
AOX+UVA	16.1	13.3	13.7	9.0	4.9	6.4	3.7	3.9	38.2	23.2	16.2
All	20.2	33.6	33.1	59.9	63.7	19.5	31.0	23.5	32.5	23.7	18.4
black											
HALS	6.3	5.7	5.8	–	–	16.2	20.8	21.1	2.1	2.4	2.5
UVA	0.8	1.1	1.0	1.3	0.9	2.7	0.7	1.5	2.3	1.4	1.2
AOX	11.4	18.4	14.2	6.3	8.9	4.4	1.8	3.1	15.3	12.0	2.3
HALS+UVA	25.0	47.3	22.9	38.8	38.2	9.2	18.1	22.9	3.9	4.5	3.3
HALS+AOX	40.3	45.0	38.6	102.5	89.4	16.3	22.2	38.2	60.3	32.1	46.2
AOX+UVA	15.5	19.8	12.5	8.4	15.0	4.5	2.0	4.3	61.0	10.7	5.6
All	25.2	31.5	30.0	62.9	90.8	14.9	23.6	38.5	30.1	8.9	7.4

Table 9 Extinction constants of residual stabilities for Xenotest and desert aging and equivalence of both methods

Stabilizer	poly(ester-urethane) clear			poly(ester-urethane) black		
	a_X/period^{-1}	a_D/year^{-1}	e/period year^{-1}	a_X/period^{-1}	a_D/year^{-1}	e/period year^{-1}
none	0.500	1.915	3.8	0.388	2.150	5.5
HALS	0.111	0.287	2.6	0.420	–	–
UVA	0.380	1.492	3.9	0.267	1.506	5.6
AOX	0.461	3.156	6.8	0.246	1.859	7.6
HALS+UVA	0.234	0.782	3.3	0.263	1.435	5.5
HALS+AOX	0.169	0.347	2.1	0.368	0.810	2.2
UVA+AOX	0.570	3.402	6.0	0.359	3.074	8.6
All	0.323	0.235	0.7	0.312	0.572	1.8
	poly(ether-urethane) clear			poly(ether-urethane) black		
none	0.104	0.431	4.2	0.101	0.718	7.1
HALS	0.016	0.087	5.5	0.060	0.641	10.7
UVA	0.161	0.815	5.1	0.176	0.847	4.8
AOX	0.162	0.669	4.1	0.159	0.804	5.0
HALS+UVA	0.060	0.381	6.4	0.088	0.314	3.6
HALS+AOX	0.016	0.145	9.2	0.068	0.353	5.2
UVA+AOX	0.145	0.661	4.6	0.156	0.738	4.7
All	0.049	0.321	6.5	0.045	0.284	6.3
	poly(acrylic-urethane) clear			poly(acrylic-urethane) black		
none	0.098	0.447	4.6	0.075	0.420	5.6
HALS	0.055	0.239	4.3	0.056	0.295	5.3
UVA	0.153	0.775	5.1	0.126	0.703	5.6
AOX	0.135	0.899	6.7	0.103	0.912	8.9
HALS+UVA	0.076	0.527	6.9	0.057	0.502	8.8
HALS+AOX	0.082	0.420	5.1	0.134	0.550	4.1
UVA+AOX	0.139	0.767	5.5	0.178	0.946	5.3
All	0.127	0.689	5.4	0.163	0.857	5.2

onism of stabilizers. The stabilizer effectiveness introduced by Eq. (9) offers the possibility of quantitative characterization of the stabilizer synergism. If there is no interaction between the stabilizers in the mixture, the resulting stabilizer effectiveness should be a weighed average mean of the effectiveness of single stabilizers. The statistical weights are equal to mass fractions of individual additives in the stabilizer mixture. Thus, the calculated stabilizer effectiveness, AEX_{calcd}, can be expressed as follows:

$$AEX_{\mathrm{calcd}} = \sum_{\mathrm{i}} w_{\mathrm{i}} AEX_{\mathrm{i}} \qquad (10)$$

where w_{i} is the mass fraction of a single additive in the stabilizer mixture and AEX_{i} is the corresponding AEX value of the additive. For the evaluation of the synergism or antagonism, we introduce here the S-factor:

$$S = \frac{AEX - AEX_{\mathrm{calcd}}}{AEX_{\mathrm{calcd}}} 100\% \qquad (11)$$

A positive value of S-factor indicates the synergism taking place in the stabilizer mixture meanwhile a negative value is an indication of antagonism.

The stabilizer effectiveness determined for individual stabilizers and for their mixtures for 180°C and the values of AEX_{calcd} are given in Table 10. The S-factors of the stabilizer mixtures are listed in Table 11. It can be seen that the S-factor depends on the type of resin, weathering dose as well as on the combination of additives applied. For ETH and ACR systems, a general trend is an increase of S-factor with the weathering dose both for Xenotest and desert weathering (some exceptions can be seen for black-pigmented ACR). For EST, the trend is opposite. The antagonism is indicated mainly for Xenotest weathering of EST stabilized with HALS+AOX and with the mixture of all stabilizers. The antagonism is indicated also for almost all unaged ETH systems.

The values of S-factors are obtained from the treatment of experimental data so that they convey

Table 10 Measured and calculated antioxidant effectiveness at 180°C for various stabilizers and various aging stress

Stabilizer	*AEX*										
	EST					ETH			ACR		
Clearcoat	0	X2.5	X5	D0.5	D1	0	X5	D1	0	X5	D1
HALS	9.7	30.1	46.4	28.1	32.4	21.7	43.1	35.9	1.2	2.1	2.0
UVA	–0.2	–0.1	0.7	0.0	0.1	2.6	0.5	0.2	1.8	0.3	0.2
AOX	12.8	12.5	20.0	6.9	6.0	4.5	0.9	2.3	12.2	7.6	1.4
HALS+UVA	19.7	37.4	59.0	42.7	39.3	18.8	28.3	20.8	2.5	3.4	2.0
HALS+AOX	5.8	14.7	21.0	17.9	16.5	11.3	22.3	17.5	14.9	17.6	15.7
AOX+UVA	7.6	6.2	6.4	4.0	2.0	2.7	1.4	1.4	18.6	11.1	7.6
All	9.6	16.3	16.0	29.4	31.3	9.2	15.0	11.3	15.7	11.4	8.7
Black											
HALS	5.3	4.7	4.8	–	–	15.2	19.8	20.1	1.1	1.4	1.5
UVA	–0.2	0.1	0.0	0.1	–0.1	1.7	–0.3	0.5	1.3	0.4	0.2
AOX	10.4	17.4	13.2	5.3	7.9	3.4	0.8	2.1	14.3	11.0	1.3
HALS+UVA	24.0	46.3	21.9	37.8	37.2	8.2	17.1	21.9	2.9	3.5	2.3
HALS+AOX	19.6	22.0	18.8	50.7	44.2	7.7	10.6	18.6	29.7	15.6	22.6
AOX+UVA	7.2	9.4	5.8	3.7	7.0	1.7	0.5	1.6	30.0	8.6	2.3
All	12.1	15.3	14.5	31.0	44.9	6.9	11.3	18.8	14.6	6.1	3.2
	AEX calculated										
	EST					ETH			ACR		
Clearcoat	0	X2.5	X5	D0.5	D1	0	X5	D1	0	X5	D1
HALS+UVA	6.7	21.0	32.7	19.7	22.7	15.9	30.3	25.2	1.4	1.6	1.4
HALS+AOX	11.3	21.3	33.2	17.5	19.2	13.1	22.0	19.1	6.7	4.8	1.7
AOX+UVA	6.3	6.2	10.4	3.5	3.0	3.6	0.7	1.2	7.0	4.0	0.8
All	9.8	16.7	26.4	13.3	14.4	10.2	15.6	13.7	6.8	4.6	1.4
Black											
HALS+UVA	3.6	3.3	3.4	0.1	0.0	11.2	13.7	14.2	1.1	1.1	1.1
HALS+AOX	7.8	11.1	9.0	2.7	4.0	9.3	10.3	11.1	7.7	6.2	1.4
AOX+UVA	5.1	8.8	6.6	2.8	3.9	2.5	0.2	1.3	7.8	5.7	0.7
All	7.0	10.4	8.3	2.7	3.9	7.3	7.3	8.1	7.7	6.1	1.2

Table 11 Synergism expressed by the *S*-factor for various stabilizer mixtures and various aging stress

Stabilizer	*S*-factor/%										
	EST					ETH			ACR		
Clear	0	X2.5	X5	D0.5	D1	0	X5	D1	0	X5	D1
HALS+UVA	192	78	81	117	73	18	–6	–17	88	114	42
HALS+AOX	–49	–31	–37	2	–14	–14	1	–8	123	263	823
AOX+UVA	20	0	–39	16	–36	–24	105	17	165	181	861
All	–2	–3	–39	121	118	–10	–4	–18	132	148	508
Black											
HALS+UVA	562	1286	544	–	–	–26	25	55	152	218	111
HALS+AOX	151	99	109	1809	1018	–18	3	68	286	151	1535
AOX+UVA	43	7	–13	32	79	–31	107	26	283	51	212
All	72	47	75	1045	1039	–5	56	130	88	1	167

Table 12 Protection factors of the black pigment at 180°C for unstabilized polyurethanes subjected to various aging stress

EST					ETH			ACR		
0	X2.5	X5	D0.5	D1	0	X5	D1	0	X5	D1
1.32	1.47	2.65	1.37	0.85	1.33	1.38	0.67	1.05	1.31	1.11

some error. We estimate that a difference of 20% between two values of *S*-factors is not very significant. However, as seen from Table 11, the values of *S*-factors are several hundred or thousand per cent so that the synergism can be evaluated with a satisfactory reliability.

Effect of the black pigment

The resin for black-pigmented PUR samples is obtained by the addition of 10 mass% of the black paste to the amount of resin. Influence of the added black pigment itself on the polyurethane stability can also be evaluated. The protection factors of black pigment have been calculated using Eq. (4) where t_i(stab) and t_i(unstab) are the OITs for the black-pigmented and clearcoat systems, respectively. The values of protection factors of the black pigment are shown in Table 12. It can be seen that, for unstabilized samples, the black pigment has a slightly stabilizing effect for the unexposed samples and the samples exposed in Xenotest. The situation is different for the samples exposed to desert weathering where the black pigment has a slight pro-degradation effect. This can be due to different degradation mechanisms in the both weathering methods.

For the stabilized systems, the protection factors of clearcoat systems are mostly higher than the corresponding values for the black-pigmented systems. The black pigment decreases the stabilizer effectiveness for EST and ETH as seen from Table 10. For ACR, the stabilizer effectiveness of black-pigmented systems is roughly on the same level as for the clearcoat systems. From *S*-factors in Table 11 for EST and ETH it can be seen that the black pigment increases the synergism. For ACR, there is no clear trend.

Conclusions

Thermooxidation of poly(ester-urethanes), poly(acrylic-urethanes) and poly(ether-urethanes) has been studied by DSC. The samples were clearcoat and black-pigmented paints, unstabilized and stabilized with HALS, UV absorber and antioxidant, exposed to various doses of weathering in Xenotest and in Arizona desert.

DSC is a powerful tool to evaluate the thermooxidation stability of polyurethanes. The technique failed in the determination of oxidation induction times at constant temperature. On the other hand, the measurements with linear heating provided readily the oxidation onset temperatures. From the dependences of OOT on heating rates, the kinetic parameters describing the dependence of the lengths of induction periods on temperature can be obtained. These kinetic parameters enable to calculate the oxidation induction times for a temperature of interest.

Based on the values of oxidation induction times, we introduced a set of criteria for the evaluation of polymer stability. In our previous papers the protection factor and the effectiveness of the stabilizer have been suggested [9, 12]. These two criteria characterize the stability of the system polymer+additives as a whole. It is advisable to use these two criteria instead of the values of induction periods since the induction period depends strongly on temperature, as seen from Eq. (3). For the evaluation of the protection factor and the effectiveness of stabilizers by Eqs (4) and (9), a ratio of the induction periods for stabilized and unstabilized polymer is used so that the dependence is much weaker.

Further criterion is the residual stability which was defined in [8, 10]. The main idea is that a material has granted a determinate stability. During ageing, the stability is depleted so that the stability can be divided into two parts, i.e. the depleted and residual stabilities. Determination of the value of depleted stability could be hardly feasible due to variety and variability of the factors bringing about the ageing. On the other hand, the residual stability can be determined with a satisfactory reliability in the accelerated thermooxidation tests and can be calculated using Eq. (5). The residual stability decreases with ageing dose. The extinction coefficient occurring in Eq. (6) represents a criterion for the evaluation of the susceptibility of a material to ageing. The values of extinction coefficients enable to calculate the equivalence between two ageing methods by Eq. (5). The last criterion, characterizing the interactions in a mixture of stabilizers (or, said more generally, additives) is the *S*-factor. The *S*-factor enables to detect the synergism or antagonism occurring in a mixture of stabilizers.

The criteria itemized above enable to optimize the mixture of stabilizers (additives) used in the material preparation, to find materials with the lowest susceptibility to ageing or to choose a proper method of accelerated weathering for the determination of material lifetime.

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